Optical constants of ice Ih crystal at terahertz frequencies

Chun Zhang

Department of Physics, University of California at Berkeley, Berkeley, CA 94720

and Materials Sciences Division, Lawrence Berkeley National laboratory, Berkeley, CA 94720

Kwang-Su Lee and X. –C. Zhang

Department of Physics, Rensselaer Polytechnic Institute, Troy, NY 12180

Xing Wei and Y. R. Shen[(a)]

Department of Physics, University of California at Berkeley, Berkeley, CA 94720

and Materials Sciences Division, Lawrence Berkeley National laboratory, Berkeley, CA 94720

Abstract

Terahertz time-domain spectroscopy was used to measure the refractive indices of Ih crystalline ice in the frequency range of 0.25–1.0 THz. With increasing frequency, the real part, *n*', of the refractive index increases from 1.787 to 1.793 at 243K, and the imaginary part, *n*", increases from 0.005 to 0.020. The temperature dependence of *n*' is less than 0.01%/K and that of *n*" is ~1%/K. Our results connect smoothly to the data of Matsuoka *et al.* in the microwave range and the data in the far IR range, and can be well described by the existing theoretical models.

[a)]Email: shenyr@socrates.berkeley.edu

Ice is one of the most common materials on earth and in outer space, and has important relevance to a large number of diverse fields such as astronomy, geophysics, chemical physics, life sciences, etc. Consequently, it has been extensively studied for centuries.[1-3] The dielectric properties of ice, in particular, have been investigated in detail covering the range from uv, visible and infrared, down to microwave frequencies.[4-9] They are dominated at the low-frequency end by the molecular reorientation mechanism which is made possible by the presence of bonding defects in the crystal. Debye relaxation of reorientation causes the dielectric loss to decrease with increasing frequency. As the frequency moves into the THz region, contribution from lattice vibrations become gradually more significant. THz spectroscopy on ice is of great importance to astrophysics. For example, reflection spectra from the Saturn rings showed that the rings were made of ice or covered in water frost, and the exact model depends on the dielectric constant of ice.

The published work on dielectric constants or refractive indices of ice in the 0.1−1.0 THz region is however limited. The only available experimental data to date were reported by Mishima *et al.*[10] and Whalley and Labbé[11], who measured the absorption coefficients of ice in the 0.25−0.75 and 0.75−1.3 THz ranges, respectively, using the conventional far-infrared spectroscopic technique with a grating monochromator and a bolometer. The values of the imaginary part of the refractive index ($\tilde{n} = n' - in''$) deduced from their measurements were found to be 30% lower than n'' extrapolated from curve fitting to the microwave data in the 10−100 GHz range[12-16] by Matsuoka *et al.*[16] The real part, n', of the refractive index in the 0.1−1.0 THz range is expected to be 1.78±0.02 from the extrapolation, but this has not yet been verified by experiment. The recent development of THz time-domain spectroscopy (TDS) with femtosecond laser pulses has permitted more accurate measurements of complex refractive indices of materials in the THz range. Therefore it should be interesting to apply the technique to the study of crystalline ice. We report here the results of our THz-TDS spectroscopic measurement of ordinary refractive indices of ice in the frequency range of 0.25–1.0 THz and temperature range of 239–264 K.

The single crystals of hexagonal ice (Ih) used in our experiment were grown by the Bridgeman method[17] from triply distilled, de-ionized water (with a resistivity higher than 18.3 MΩ-cm) at a rate of ~1 μm/sec. Each sample was prepared by orienting and cutting a crystal to the desired length; the c-axis of the crystal was oriented perpendicular to the surfaces to within 3°. The sample was then sandwiched between two fused silica plates and mounted in a sealed chamber with temperature variable from 233–273 K and controllable to ±0.2 K.

The THz-TDS experimental setup has been described in detail elsewhere.[18] In brief, the THz pulses were generated by ultrashort current pulses on a GaAs crystalline surface switched on by the excitation of femtosecond pulses with a repetition rate of 80 MHz from a Ti:sapphire laser oscillator. They had an average power of ~0.1 μW. These pulses were collimated and focussed, and sent through the sample with a beam cross section of 1 mm^2. The time-resolved field variation, $E(t)$, of the transmitted pulse was then detected via electro-optical effect in a ZnTe crystal using the lock-in detection scheme. An example is shown in Fig. 1. A beam intensity stabilizer was used to reduce laser intensity fluctuations to ~0.1%. The maximum signal-to-noise ratio achieved in the experiment was 10^5.

Fourier transform of $E(t)$ gives both the amplitude $A(f)$ and the phase $\varphi(f)$ of the field component in the frequency (f) domain. To avoid complications of characterizing the input THz pulses, we conducted the measurement on two samples of different lengths situated in the same chamber. The complex refractive index $\tilde{n}(f)$ can then be deduced from the following equations with the experimentally determined $A_i(f)$ and $\varphi_i(f)$ (with i = 1 and 2) for the two crystals.

$$\begin{aligned} \frac{A_2}{A_1} &= \exp\left[-\frac{2\pi f}{c} n''(d_2 - d_1)\right] \\ \varphi_2 - \varphi_1 &= \frac{2\pi f}{c} n'(d_2 - d_1) \end{aligned} \tag{1}$$

where d_1 and d_2 denote the lengths of the two crystals. Note that the lengths change with temperature due to thermal expansion.

The deduced values of n' and n'' for ice at 243 K from our measurement are presented in Table I and plotted in Fig. 2. With the frequency increasing from 0.25 to 1.0 THz, n' increases from 1.787 to 1.793 and n'' increases from 0.005 to 0.020. Within the temperature range of 239–264 K, the variation of n' is hardly perceptible, indicating that $(dn'/dT)/n'$ is less than 10^{-4}/K, but n'' increases linearly with temperature (depicted in Fig. 3) with $(dn''/dT)/n''$ = ~1×10^{-2}/K.

Fig. 2 plots our results together with those reported by others in the range of 10^9 to 10^{13} Hz. For n', our THz data bridge smoothly the gap of the existing data in the far IR and microwave regions. For n'', our data points fall nicely on the curve (solid line) used by Matsuoka *et al.*[16] to fit their microwave data. The results of Mishima *et al.*,[10] Whalley *et al.*,[11] and Koh[15] appear to lie 30% below the curve and that of Mätzler *et al.*[12] 30% above.

The fitting curve of Matsuoka *et al.* in Fig. 2(b) is described by[16]

$$n'' = \frac{1}{2n'}\left[(A/f) + Bf^{C}\right] \qquad (2)$$

with $A = 4.044\times10^{-5}$ GHz, $B = 3.654\times10^{-5}$ GHz^{-1}, and $C = 1.083$ at 243 K. Although it appears to be a good representation of n'' of ice in the frequency range between 40 GHz and 1 THz, the physical meaning of the coefficients B and C is still not clear.

The existing theoretical models for dielectric properties of ice indicates that at low frequencies, the dielectric constant or refractive index is dominated by contribution from defect-initiated molecular reorientation. The high frequency tail of Debye relaxation extends the influence of reorientation into the microwave region, contributing to the A term in Eq. (2).[16] In the microwave range and higher, excitation of a low-frequency difference combination band becomes important, yielding a term in n'' proportional to f.[10] This mechanism is the dominant contribution in the frequency range we have studied. Farther up in frequencies (above 1 THz), the low-frequency tails of the low-lying infrared phonon absorption bands should play an increasingly important role.[6] Whalley and coworkers[11] also proposed excitations of acoustic phonons as a mechanism that contributes to n'' with a f^3 frequency dependence, but this mechanism is only operative in polycrystalline ice with nanometer-size particles. Thus, in the frequency range we are interested, only the first two mechanisms are important. Therefore, following the theoretical models,[10,16] we can write

$$n'' = C_1/f + C_2 f$$

with

$$C_1 = A/2n' \qquad (3)$$

$$C_2 = \frac{1}{4\pi c}\frac{B_0}{T}\frac{e^{hc\nu_0/kT}}{(e^{hc\nu_0/kT}-1)^2}\frac{1}{\nu_0^2}$$

Here, A is the same constant appearing in Eq. (2), $B_0 = 1.391\times10^5$ cm^{-1}K and $\nu_0 = 233$ cm^{-1}.[10] To compare with the experimental results, we plot Eq. (3) with $T = 243$ K in Fig. 2(b) (dashed curve). It is seen that the calculation from the theoretical models fits quite well with the results of Matsuoka *et al.*[16] and ours except for a discrepancy of less than 40% towards 1 THz. This could result from approximation in calculating C_2 in the theoretical model.[10]

Eq. (3) also allows us to derive the temperature dependence of n". In the frequency range of our interest, n" is dominated by the C_2 term. For $T = 200-273$ K, we can approximate the temperature dependence of C_2 by a linear line, which takes the form

$$C_2 = 1.256\times10^{-14} + 6.8\times10^{-17}(T-243) \quad \text{in Hz}^{-1}. \tag{4}$$

Around 243K, this leads to a predicted (dn"/dT)/n" = 5.4×10^{-3}/K, which agrees with the experimental result within a factor of two.

In conclusion, we have shown that the THz-TDS technique can be used to measure accurately the refractive indices of crystalline ice in the THz range. Our 0.25−1.0 THz results bridge the gap between the microwave and the far IR regions. They agree very well with the curve extrapolated from the microwave data of Matsuoka *et al.*, and provide an assessment of the reliability of the experimental data of others. It is found that the existing theoretical models describe well the refractive indices in this region. Extension to frequencies higher than 1 THz will be desirable.

We are grateful to Prof. Lei Xu (Fudan University) and Dr. Fengguo Sun (Rensselaer Polytechnic Institute) for helpful discussions. This work was supported by the U.S. Department of Energy under the Contract No. DE-AC03-76SF00098 (UC Berkeley) and U.S. National Science Foundation (Rensselaer).

Tables:

Table I: Complex refractive indices of crystalline ice (Ih) at 243 K. The measured values of *n*” of Matsuoka’s (5−39 GHz) and ours (0.25−1.00 THz) are listed together with those calculated from Eqs. (2) and (3) for comparison. The errors of our measured values are ±0.002 for *n*’ and ±0.0005 for *n*”.

frequency (THz)	Measured *n*’	Measured *n*”	Calc. of *n*” from Eq. (2)	Calc. of *n*” from Eq. (3)
0.0050		6.32×10^{-5}	6.09×10^{-5}	6.51×10^{-5}
0.0100		1.21×10^{-4}	1.25×10^{-4}	1.27×10^{-4}
0.0330		3.61×10^{-4}	4.53×10^{-4}	4.15×10^{-4}
0.0390		5.91×10^{-4}	5.43×10^{-4}	4.90×10^{-4}
0.2500	1.787	0.0045	0.0041	0.0031
0.3125	1.786	0.0057	0.0052	0.0039
0.3750	1.786	0.0071	0.0063	0.0047
0.4375	1.786	0.0087	0.0074	0.0055
0.5000	1.786	0.0098	0.0086	0.0063
0.5625	1.787	0.0109	0.0098	0.0071
0.6250	1.788	0.0119	0.0110	0.0079
0.6875	1.789	0.0129	0.0121	0.0086
0.7500	1.789	0.0140	0.0133	0.0094
0.8125	1.790	0.0147	0.0145	0.0102
0.8750	1.791	0.0161	0.0158	0.0110
0.9375	1.793	0.0169	0.0170	0.0118
1.0000	1.793	0.0205	0.0182	0.0126

References:

[1]P. V. Hobbs, Ice Physics, Clarendon Press, Oxford, 1974.

[2]J. S. Wettlaufer, J. G. Dash, and N. Untersteiner, Ice Physics and the Natural Enviroment, Springer, Berlin, 1999.

[3]V. F. Petrenko and R. W. Whitworth, Physics of Ice, Oxford University Press, Oxford, 1999.

[4]H. E. Merwin, in Int. Crt. Tabl. **7**, 16 (1930).

[5]C. Sauberber, Wett. Leben **2**, 193 (1950).

[6]J. E. Bertie, H. J. Labbé, and E. Whalley, J. Chem. Phys. **50**, 4501 (1969).

[7]W. M. Irvine and J. B. Pollack, Icarus **8**, 324 (1968).

[8]S. Evans, J. Glaciol. **5**, 773 (1965).

[9]S. G. Warren, Appl. Opt. **23**, 1206 (1984).

[10]O. Mishima, D. D. Klug, and E. Whalley, J. Chem. Phys. **78**, 6399 (1983).

[11]E. Whalley and H. J. Labbé, J. Chem. Phys. **51**, 3120 (1969).

[12]C. Mätzler and U.Wegmüller, J. Phys. D **20**, 1623 (1987); **21**, 1660(E) (1988).

[13]S. Fujita, S. Mae, and T. Matsuoka, Ann. Glaciol. **17**, 276 (1993).

[14]S. Surdyk and S. Fujita, Geophys. Res. Lett. **22**, 965 (1995).

[15]G. Koh, Geophys. Res. Lett. **24**, 2311 (1997).

[16]T. Matsuoka, S. Fujita, and S. Mae, J. Appl. Phys. **80**, 5884 (1996).

[17]R. A. Brown, J. Kelzer, U. Stelger, and Y. Yeh, J. Phys. Chem. **87**, 4135 (1983).

[18]P. Y. Han, M. Tani, M. Usami, S. Kono, R. Kersting, and X.-C. Zhang, J. Appl. Phys., **89**, 2357 (2001).

Figure Captions:

FIG. 1: Measured temporal spectra of original THz waveform, the transmitted THz waveform through the empty chamber, and the transmitted THz waveform through the chamber with an ice sample. For clearance of the plot, the latter two spectra are shifted vertically, and their time delays are omitted.

FIG. 2: (a) real and (b) imaginary refractive indices of ice in the range of 10^9–10^{13} Hz. Experimental data points obtained by various groups are labeled by the first author's names in the graph. The solid (dashed) line in (b) is calculated from Eq. (2) (Eq. (3)) at 243 K.

FIG. 3: Temperature dependence of the imaginary refractive index *n*" of ice at four different frequencies: 0.25, 0.50, 0.75, and 1.00 THz.

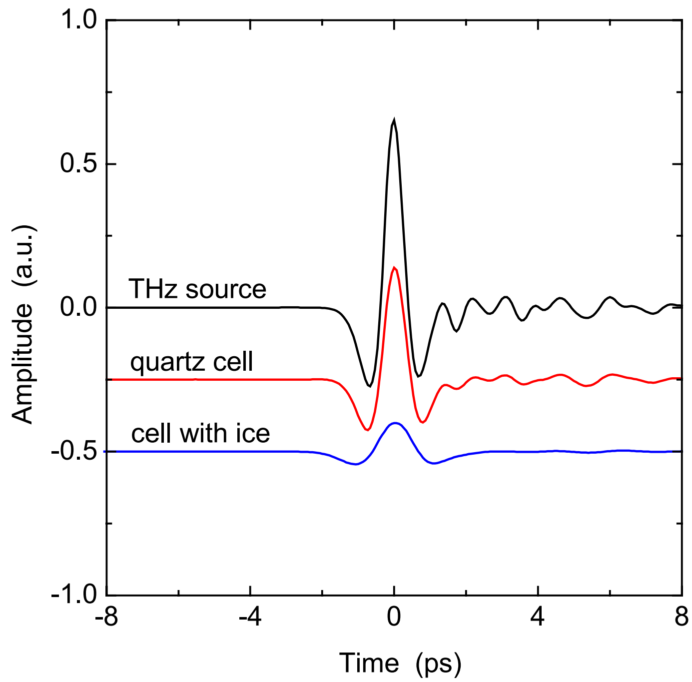

Fig. 1 / Zhang *et al.*

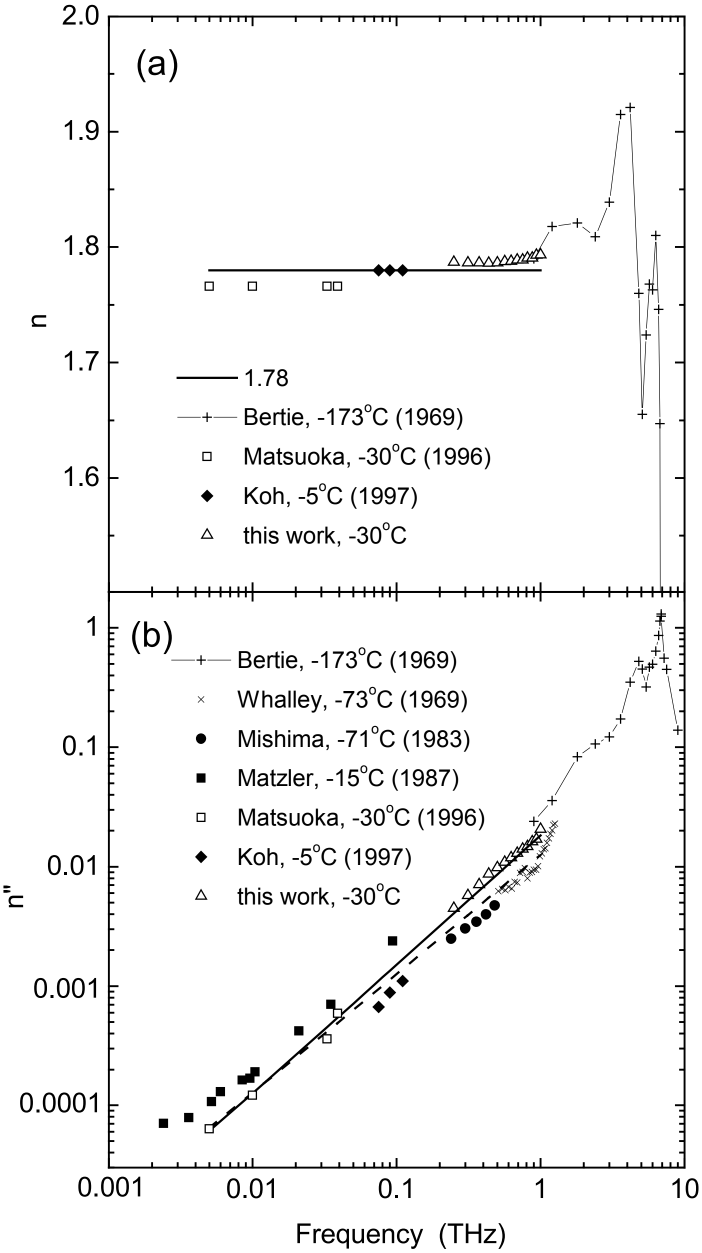

Fig. 2 / Zhang *et al*.

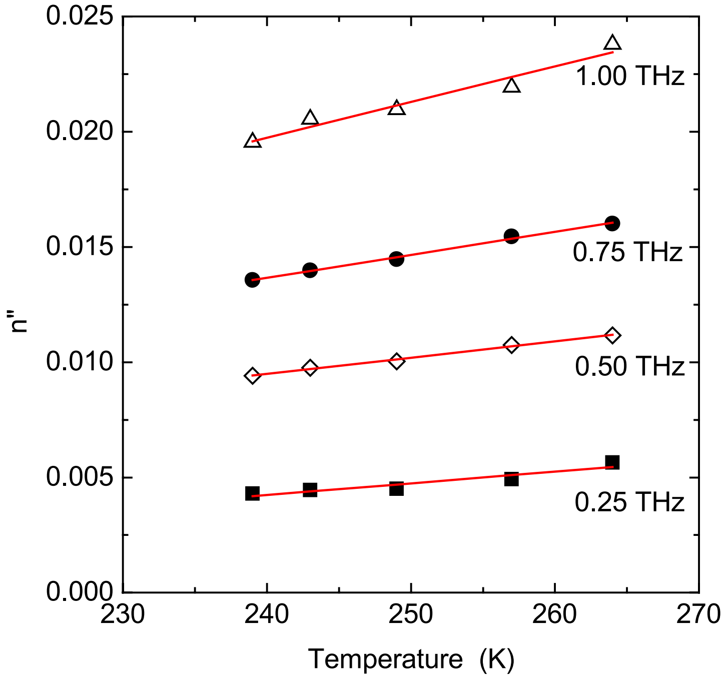

Fig. 3 / Zhang *et al.*